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# Review on Schiff bases and their metal complexes as organic photovoltaic materials

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ABSTRACT

Solar energy sources, having the potential to provide energy services with zero emissions of air pollutants, have become more economically attractive with technological improvements. Organic Solar cells promise to be a significant contributor to our future energy system with suitable efficiencies and low cost. The foundation, basic principles, material requirements and device operation mechanism of organic solar cells has been already reviewed by various authors. This paper highlights the use of Schiff bases and their metal complexes as Photovoltaic materials. Schiff bases having potential Photovoltaic characteristics are also discussed in this paper. Major developments in this field over the past few years and recent research have also been briefly discussed.



**Contents**



## 1. Introduction

The ever-swelling exploitation of fossil fuels by humans has ruined the environment, and has made everyone realize now that, return to pre-industrial era is impossible. To solve our problems, a sustainable development is needed. The use of novel technology to harness renewable energy efficiently to supplement our traditional energy must be designed. Renewable energy sources have the potentiality of providing energy services with zero or close proximity to zero emissions of both air pollutants and green house gases. Among the various renewable energy sources available, solar energy conversion systems have attracted much attention by the researchers and engineers, due to their abundant availability of their source, the solar radiations. The Earth receives 120,000 TW of electromagnetic radiation through solar irradiation, and will continue till the death of our Sun some 5 billion years from now. Beginning with a hint from nature, A.E. Becquerel in the year 1839, for the first time observed the photovoltaic effect [1]. Photovoltaic devices convert solar energy directly into electrical energy without any emissions. For a single gigawatt—hour of electricity generated by solar photovoltaics, more than 1000 t of $CO_2$ emission is being reduced. Since the discovery of photovoltaic effect research has bloomed in this field, with development of photovoltaic devices using organic, inorganic and hybrid materials. Though inorganic materials have so far been very promising in the development of this field, organic materials as photovoltaics are also showing great hope.

Higher cost and complex production procedure involved with the inorganic photovoltaic devices, has crippled its extensive use in domestic and other commercial applications. However, organic photovoltaic devices with their low cost, easy reproducibility and

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non-toxic nature tend to be potential future energy source globally. Though organic materials are cheaper and have ease of reproducibility, their efficiencies have not yet reached the level deemed as necessary for commercial use. Newer organic materials that could overcome the drawbacks faced by the present conventional materials, is the latest trend on research. Schiff base compounds have been tried as substituent, and their possibilities have also been reported by various researchers.

In this context, this paper brings in the various works done in this field, and discusses their prospects. Schiff base and their metal complexes that have optoelectic properties and could be used in photovoltaics with improvements have been listed. Schiff base compounds are very promising because of their biodegradability, non-toxicity, good electrical conductivity in conjugated compounds, and cheaper and easier production.

## 2. History

After the discovery of the photovoltaic effect by A.E. Becquerel, in 1906, Pochettino observed photoconductivity for the first time in anthracene, an organic compound [2]. With this as the starting note, photoconductivity of various organic materials was studied in the 1950s with the aim of using them as photoreceptors. It was during this time that, in the year of 1959, Kallmann and Pope observed photovoltaic effect in a single crystal of anthracene sandwiched between two identical electrodes when it was illuminated from one side. Later on, photovoltaic effect was observed in many common dyes, such as methylene blue and was also observed in many important biological molecules such as carotenes, chlorophylls and other porphyrins, as well as the structural related phthalocyanines (PC) [3,4].

The first generation of organic photovoltaic solar cells were based on single organic layers sandwiched between two metal electrodes of different work functions [4]. The power conversion efficiencies reported were generally poor (in the range of 0.001 to 0.01%), but reached remarkable 0.7% for merocyanine dyes in the early days [5]. In this case, the organic layer was sandwiched between a metal–metal oxide and a metal electrode, thus improving the Schottky-barrier effect [6]. A major breakthrough in the field came in 1986 when Tang fabricated a thin film, two-layer organic photovoltaic cell, from copper phthalocyanine and a perylene tetracarboxylic derivative and discovered that the output power could be greatly increased if two materials were used instead of just one [7]. It was the first known heterojunction organic solar cell.

Later on the organic solar cell development gained momentum in the past years with the conversion efficiencies reaching 4%, with the development of new designs such as, (i) the evaporated bilayer devices [8,9] in which thin film layers are coated through thermal evaporation process; (ii) the bulk heterojunction polymer–fullerene devices [10–17] in which the donor polymers are blended with the fullerene and coated in between the electrodes; (iii) the co-evaporated molecular devices [18–21] in which two materials that are to be used for the application are mixed and evaporated together; and (iv) the organic–inorganic hybrid devices [22–24], which are at present the more efficient type of devices. Recent progress achieved using organic single-crystal, multilayered thin film and blended network technologies permit one to expect a very fast increase in the conversion yield of organic solar cells. This will possibly make them a competitive alternative to the various forms of silicon cells.

## 3. Operation of organic solar cells

The organic solar cells produce electric energy directly from solar radiation through a chain process. The operational mechanism of these devices is illustrated in Figs. 1 and 2.

These are the productive events of the PV process.

(i) Photons from the solar radiation enter inside the device and are absorbed by an electron in the highest occupied molecular orbital (HOMO) of the organic material.
(ii) The electron which has absorbed the photon, gets excited to the lowest unoccupied molecular orbital (LUMO), creating an exciton (bound electron–hole pair).
(iii) The created exciton diffuses to the interface of two materials, the electron donor and electron acceptor, and carriers are generated from the exciton dissociation.
(iv) The generated carriers are collected by the electrodes and driven into the external circuit to produce power and do work.

## 4. Challenges

Though organic solar cells have reached the benchmark of 10% efficiency [26], they still face a number of obstacles that are preventing them from moving beyond the laboratory. After the demonstration of the first donor (D)–acceptor (A) heterojunction by Tang [7], there has recently been a rapid increase in cell efficiency. The simultaneous researches in the field of organic LEDs have influenced the development of efficiencies of organic solar cells since organic light-emitting devices often employ materials and device structures that have direct application to light detection [27].

To reach an approximate upper bound of obtainable efficiency of 20%, at 100% conversion efficiency across the visible spectrum, Stephen R. Forrest has listed few challenges that must be overcome [27].

- The cell must have an efficient response across the entire solar spectrum.
- Couple most of the light into active heterojunction by surpassing the exciton diffusion bottleneck in tandem solar cells.
- Reduce the cell resistance in transporting the power from its generation site to the load by creating low-optical loss, high-conductivity contacts.

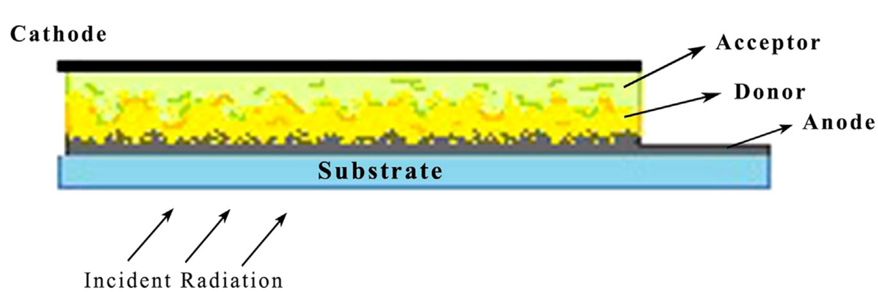



**Fig. 1.** Schematic diagram of a thin-film organic solar cell and its components.

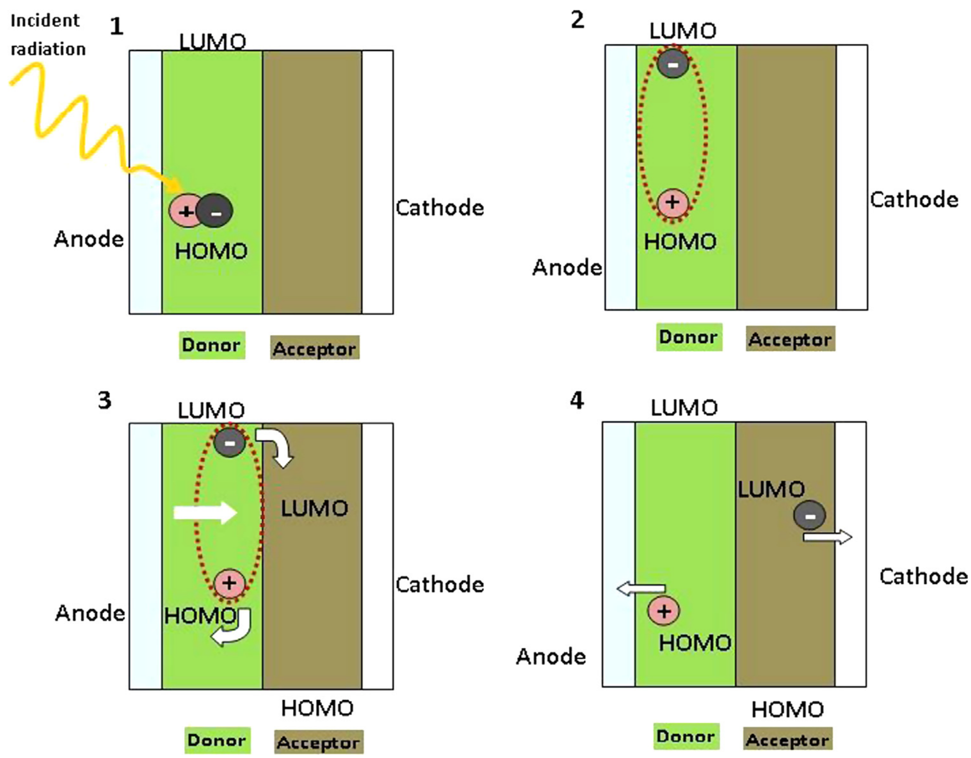



**Fig. 2.** Charge carrier generation in OPVs.

Another challenge for OPVs is that efficiencies decrease as the size of the cell increases. Increasing size of the cell results in higher sheet resistivity and greater defects in the organic films [25]. Rapid improvements in efficiency have been achieved recently by controlling these factors well; making use of the characteristic that the polymers can be designed freely with conjugated polymers. In spite of various challenges in increasing the efficiency of organic solar cells, the fact that organics can potentially transform the cost structure for generating cheap and clean renewable energy from the sun, has attracted many researchers in this field.

## 5. Schiff bases in photovoltaic devices

In 1864, German chemist Hugo Schiff developed a new class of organic compounds. These groups of compounds, imines, are often referred to as Schiff bases in his honour. Schiff bases have attracted the attention of chemists due to the ease of preparation and complexation. Conjugated Schiff base polymers and oligomers have been widely studied for the last two decades due to their excellent thermal, mechanical, electronic, optical, optoelectronic, and fibre-forming properties [28–32]. Schiff bases contain the azomethine group (–RC=N–) and are usually formed by the condensation of a primary amine with an active carbonyl compound. They are stable and can tune the ligational aspects by varying denticity and basicity. Metal Schiff base complexes have been known since the mid nineteenth century and even before the report of general preparation of the Schiff base ligands. Intensive research on the physicochemical properties and molecular structure of complexes with Schiff bases has provided interesting new results.

Extensive studies have been made on fabrication and performance of organic photovoltaic devices. Investigations have suggested that conjugated poly-Schiff bases as new semiconducting materials have good stability, electroactivity and electrical conductivity. The presence of conjugated bonding leads to electron delocalization along the polymer chain and to the possibility of high charge carrier mobility. Conjugated polymer, with metals, forms Schottky barrier. Nitro aromatic compounds are resistant to oxidative attack because of their electron-withdrawing nature. By attaching a nitro group at one end of the molecule stable compound against oxidation can be obtained. Therefore, substituting Schiff base polymers in organic solar cells will increase their performance.

Pure organic dyes have many advantages when they are used in photovoltaic devices. First of all they have higher absorption coefficients than metal complexes, and a wider range of dyes for different light absorption bands. Pure organic dyes are cost effective; their resources are unlimited, and they are also easily recyclable. There is also a great growth of interest and attention being paid in the design and synthesis of pure organic dyes because of the easier theoretical evaluation of photoelectrochemical properties and design of new pure organic dye by computer simulation than that of metal complexes [33]. Under these circumstances a few papers on pure organic Schiff bases are reviewed.

Kaya et al. [34] synthesized novel low band gap and thermally stable poly(azomethine-urethane)s (PAMUs) to investigate aliphatic and aromatic group effects on some physical properties such as thermal stability, optical and electrochemical properties. The UV–vis absorption spectra for the PAMUs are listed in Tables 1 and 2. The absorption of PU-VANDAP is little deeper into the visible range than PU-VANDAH. The PU-VANDAP has a lesser electrochemical band gap than the PU-VANDAH, which suggests that the aromatic group is more suitable for the photovoltaic purpose than aliphatic groups. Also, TGA results showed that among the synthesized PAMUs, the compound with the aromatic ring had high thermal stability than the aliphatic group. The investigation thus showed that Schiff bases with aromatic groups could be more reliable in photovoltaic applications, than their aliphatic groups.

Iwan et al. [35] reported the optical (electrical) properties of two soluble organic molecules based on azomethines with

**Table 1**
Reviewed Schiff base ligands and their metal complexes.

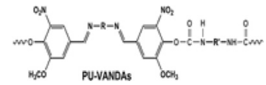
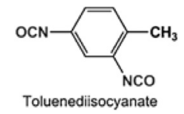
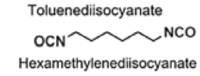
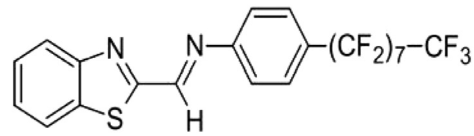
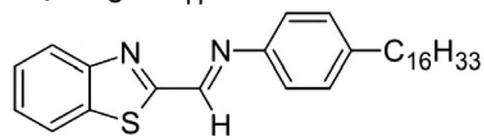
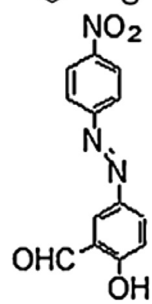
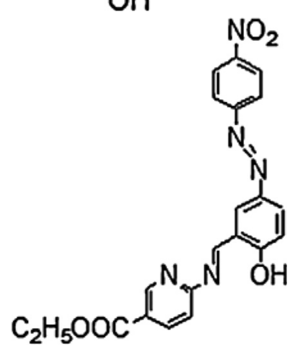
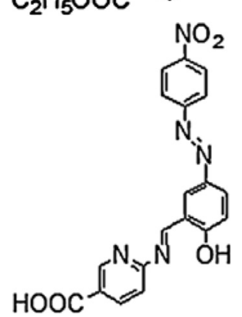
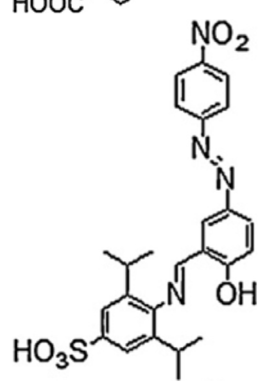
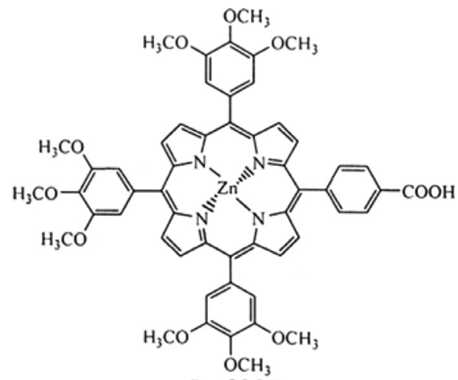
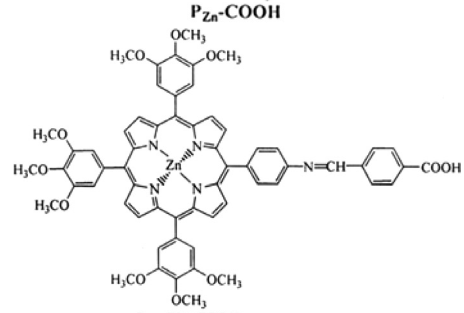
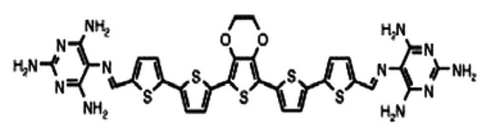
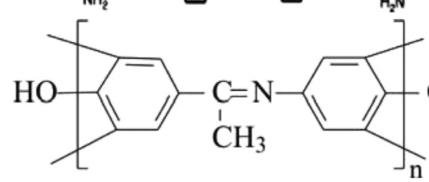
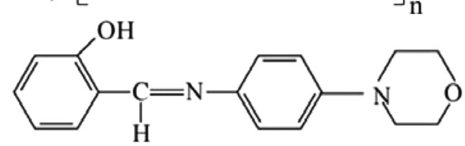
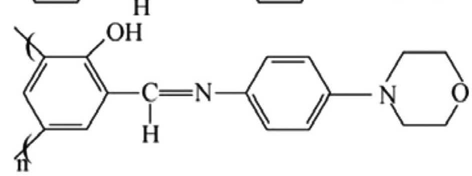
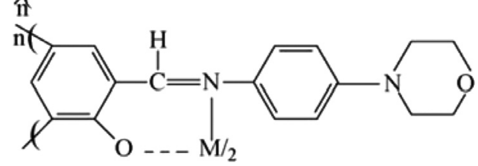
| Dyes | Abbreviations | Structure | Reference |
|---|---|---|---|
| | PU-VANDAP |     | [33] |
| | PU-VANDAH |   | [33] |
| *N*-[(*E*,*Z*)-1,3-benzothiazol-2-ylmethylidene]-4-(heptadecafluoroctyl)aniline | BTA1 |  | [34] |
| *N*-[(*E*,*Z*)-1,3-benzothiazol-2-ylmethylidene]-4-hexadecylaniline | BTA2 |  | [34] |
| 3,5-Diisopropyl-4-aminobenzenesulfonic acid | Azo dye 1 |  | [35] |
| 1-[3-(((4-Ethylcarboxylatepyridyl)imino)methyl)-4-hydroxyphenylazo]-4-nitrobenzene | Azo dye 2 |  | [35] |
| 1-[3-(((4-Carboxypyridyl)imino)methyl)-4-hydroxyphenylazo]-4-nitrobenzene | Azo dye 3 |  | [35] |
| 1-[3-(((2,6-Diisopropyl-4-sulfophenyl)imino)methyl)-4-hydroxyphenylazo]-4-nitrobenzene | Azo dye 4 |  | [35] |

**Table 1** (*continued*)

| Dyes | Abbreviations | Structure | Reference |
|---|---|---|---|
| 5-(4-Carboxyl) phenyl-10,15,20-tris (3,4,5-trimethoxylphenyl) porphyrin | $P_{Zn}$-COOH |  $P_{Zn}$-COOH | [36] |
| 5-[*p*-(4-Carboxyl benzyl idene amino)] phenyl-10, 15,20-tris(3,4,5-trimethoxy-lphenyl)porphyrin zine | $P_{Zn}$-BIA-COOH |  $P_{Zn}$-BIA-COOH | [36] |
| Poly(phenyl azomethine furane)<br>*N*,*N*′-bis(2-hydroxy-1-naphtaldehydene)-1,4-bis (*o*-amino phenilthio)butane | PPAF |  | [37]<br>[38] |
| Poly-4-[1-(4-hydroxyphenyl) ethylideneamino]phenol | P-4-HPEAP |  | [41] |
| 2-[(4-Morpholin-4-yl-phenyl)imino] methylphenol | 2-MPIMP |  | [43] |
| Oligo-2-[(4-morpholin-4-ylphenyl)imino] methylphenol | *O*-2-MPIMP |  | [43] |
| *O*-2-MPIMP-metal complexes | *O*-2-MPIMP–Cu<br>*O*-2-MPIMP–Co<br>*O*-2-MPIMP–Cd<br>*O*-2-MPIMP–Zn<br>*O*-2-MPIMP–Pb<br>*O*-2-MPIMP–Zr |  | [43]<br>[43]<br>[43]<br>[43]<br>[43]<br>[43] |

benzothiazole core (BTA1 and BTA2). The optical properties such as the UV–vis absorption and photoluminescence were measured. The UV–vis absorption values are listed in Table 2 for both the compounds (BTA1 and BTA2). The photoluminescence property of BTA1 was higher in comparison with BTA2 because of the fluorine chain present in its structure. It was inferred that fluorine atoms lower the luminescent excited state and also influence the electronic structure of the compounds by increasing the probability of radiative transition. The photovoltaic property was also determined by applying these compounds as acceptor materials in bulk heterojunction (BHJ) devices. The photovoltaic properties are presented in Table 3. The PCE of BTA1 was three times greater than BTA2, because of the presence of the fluorine atoms. It was suggested that, the compounds having polar groups like fluorine are better for photovoltaic applications.

Dincalpa et al. [36] synthesized a series of new azo dyes containing salicylaldimine with different electron-withdrawing groups. They studied the absorption and emission spectra of the

**Table 2**
UV–vis absorption spectroscopic parameters of various Schiff bases and their metal complex dyes.

| Dyes | Solution | Wavelength λ (nm) | Reference |
|---|---|---|---|
| PU-VANDAP | DMSO | 272, 335, 444 | [33] |
| PU-VANDAH | DMSO | 281, 333, 425 | [33] |
| BTA1 | Chloroform | 324 | [34] |
| | Solid state as thin film | 335 | [34] |
| BTA2 | Chloroform | 315, 355 | [34] |
| | solid state as thin film | 353 | [34] |
| Azo dye 1 | Chloroform | 359 | [35] |
| | Ethyl acetate | 356 | [35] |
| | Tetrahydrofuran | 362 | [35] |
| | 1-Butanol | 380 | [35] |
| | Water | 381 | [35] |
| Azo dye 2 | Chloroform | 379 | [35] |
| | Ethyl acetate | 373 | [35] |
| | Tetrahydrofuran | 271 | [35] |
| | 1-Butanol | 407 | [35] |
| | Water | 447 | [35] |
| Azo dye 3 | Chloroform | 378 | [35] |
| | Ethyl acetate | 370 | [35] |
| | Tetrahydrofuran | 273 | [35] |
| | 1-Butanol | 276 | [35] |
| | Water | 448 | [35] |
| Azo dye 4 | Chloroform | 267 | [35] |
| | Ethyl acetate | 277 | [35] |
| | Tetrahydrofuran | 268 | [35] |
| | 1-Butanol | 380 | [35] |
| | Water | 379 | [35] |
| $P_{Zn}$-COOH | DMF solution | 423, 559, 600 | [36] |
| $P_{Zn}$-BIA-COOH | DMF solution | 431, 564, 606 | [36] |
| PPAF | Acetone solution | 330.8, 527 | [37] |
| 4-HPEAP | Methanol and DMSO | 289 | [41] |
| P-4-HPEAP | Methanol and DMSO | 296 | [41] |
| 2-MPIMP | Methanol | 364 | [43] |
| *O*-2-MPIMP | | 367 | [43] |
| *O*-2-MPIMP–Cu | DMSO | 423 | [43] |
| *O*-2-MPIMP–Co | | 454 | [43] |
| *O*-2-MPIMP–Cd | | 435 | [43] |
| *O*-2-MPIMP–Zn | | 466 | [43] |
| *O*-2-MPIMP–Pb | | 445 | [43] |
| *O*-2-MPIMP–Zr | | 459 | [43] |
| 2-PIMP | Methanol | 332 | [44] |
| *O*-2-PIMP | | 341 | [44] |
| *O*-2-PIMP–Cu | DMSO | 384 | [44] |
| *O*-2-PIMP–Ni | | 354 | [44] |
| *O*-2-PIMP–Co | | 358 | [44] |
| *O*-2-PIMP–Cr | | 372 | [44] |
| *O*-2-PIMP–Pb | | 377 | [44] |
| *O*-2-PIMP–Zn | | 373 | [44] |

**Table 3**
Photovoltaic parameters of solar cells sensitized by Schiff bases and their metal complexes.

| Complex | $J_{sc}$ ($A\ cm^{-2}$) | $V_{oc}$ (V) | ff | η (%) | Reference |
|---|---|---|---|---|---|
| P3HT:BTA1 (1:1) | $1.47\times10^{-6}$ | $4.4\times10^{-3}$ | 0.25 | $0.2\times10^{-5}$ | [34] |
| P3HT:BTA2 (1:1) | $1.56\times10^{-6}$ | $2.4\times10^{-3}$ | 0.13 | $0.05\times10^{-5}$ | |
| P3HT:PCBM:BTA1 (1:1:1) | $1190\times10^{-6}$ | $400\times10^{-3}$ | 0.23 | 0.1 | |
| P3HT:PCBM:BTA2 (1:1:1) | $15\times10^{-6}$ | $30\times10^{-3}$ | 0.28 | $12.6\times10^{-5}$ | |
| Azo dye 3 | $0.80\times10^{-3}$ | 0.33 | 0.51 | 0.14 | [35] |
| Azo dye 4 | $0.65\times10^{-3}$ | 0.35 | 0.52 | 0.12 | |
| $P_{Zn}$-COOH | $4.0\times10^{-3}$ | 0.40 | 0.66 | 1.06 | [36] |
| $P_{Zn}$-BIA-COOH | $5.5\times10^{-3}$ | 0.49 | 0.65 | 1.75 | |
| PPAF | $0.2\times10^{-6}$ | 1.2 | 0.38 | $1.9\times10^{-2}$ | [37] |

synthesized salicylaldimine-based azo ligands in five solvents of different polarities. The optical and electrochemical properties were studied, and photovoltaic performance of DSSCs based on these new type salicylaldimine compounds was also investigated. The UV–vis absorption measurements are listed in Table 2. The absorption and emission maxima measurements show that, a remarkable bathochromic is obtained in water and 1-butanol solvents compared to the same spectra observed for the other solvents (cholorform, ethyl acetate and tetrahydrofuran). The photovoltaic properties of the azo dye **3** and azo dye **4** are presented in Table 3. These studies show that azo dye **3** responses are better than azo dye **4**, because of more effective electron injection from the LUMO level of azo dye **3** to the conduction band of $TiO_2$ through carboxylate bridge. These preliminary studies show that salicylaldimine-based azo ligands are appropriate sensitizers for coordinating with $TiO_2$ surface in DSSC applications. It was also suggested that new molecular modeling of azo dyes, which consist of donor-linker-acceptor moieties, is necessary to improve DSSC efficiency.

Tan et al. [37] synthesized two porphyrin dyes for use in dye-sensitized solar cells. The dyes comprised of the donor (porphyrin derivative) consisting of 3,4,5-trimethoxybenzaldehyde and acceptor/anchoring group (carboxyl group) but with varying p-spacer consisting of a Schiff base structure, to investigate how the structure of Schiff base affects the cell performance of devices. The UV–vis absorption (Table 2) of the two dyes ($P_{Zn}$-COOH and $P_{Zn}$-BIA-COOH) showed that, the $P_{Zn}$-BIA-COOH had a broader and stronger band and was more red-shifted than $P_{Zn}$-COOH. According to the study, the introduction of Schiff base unit at the meso positions, shifted the energy level of $E_{ox}$ (excited-state oxidation potentials) to the positive compared with the reference $P_{Zn}$-COOH, indicating a decreased HOMO–LUMO gap. The photovoltaic properties are listed in Table 3. The obtained results indicate that the cell performance of the device using porphyrin $P_{Zn}$-BIA-COOH as sensitizer outperformed the better-reported porphyrin dye. $P_{Zn}$-BIA-COOH exhibited a higher power conversion efficiency reaching 1.75% under AM 1.5 G irradiation.

Sharma et al. [38] synthesized poly(phenyl azomethine furane) (PPAF), a conjugated system of poly-Schiff base by condensation of *p*-aminobenzene with furane-2-aldehyde. The optical and electrochemical properties were studied. The UV–vis absorption was taken in acetone solvent, and a peak was obtained in the visible radiation side. The values are listed in Table 2. The photovoltaic characteristics study was done by fabricating ITO/PPAF/Al and ITO/PPAF/Ag devices made by depositing the PPAF by spin coating technique using dimethyl formamide (DMF) as solvent for PPAF. The device Al/PPAF/ITO showed a Schottky barrier at the Al–PPAF interface and ohmic contact at ITO–PPAF interface. The device Ag/PPAF/IT0 showed ohmic contact at both interfaces. These results indicate that PPAF is P-type organic semiconductor. In this device, the absorption of light in the thin layer by PPAF produce excitons which are dissociated at the Schottky barrier and the holes move towards the semiconductor (PPAF) and the electrons towards the Al electrode to give photocurrent.

Huang et al. [39] built a photovoltaic device using hydrogen-bonding terminated self-assembled monolayers (SAMs) on gold with hydrogen-bonding barbituric acid appended fullerene as electron acceptor material and melamine terminated π-conjugated thiophene-based oligomer as electron donor material. It was reported that the alteration of the gold electrode surface with self-assembled monolayers bearing hydrogen-bonding molecular recognition end groups led to a 2.5 fold-enhancement in photocurrent compared to similar systems comprising non-hydrogen-bonding $C_{60}$–oligomer systems, which is known for higher molecular-level ordering.

Although organic dye based solar cells are advantageous over inorganic photovoltaic devices in several ways, they still lack behind the later in efficiency. Pure organic dyes have low sensitizing properties for photovoltaic application as compared to the

metal complexes [40]. The emission lifetimes of their excited states are shorter, and also the conduction band of the semiconductor is far greater than the excitation level of electrons in the organic dyes [33]. On comparison, inorganic metal complex dyes fulfill certain features such as higher chemical and thermal stability, intense absorption in the visible region, strong adsorption onto the semiconductor surface and efficient injection of electrons onto the conduction band of the semiconductor, than pure organic dyes [41]. So, by including metal ions in organic compounds, photovoltaic property of the compounds improve and thus higher efficiencies can be obtained. Under these circumstances, Schiff base metal complex based photovoltaic applications are reviewed.

Kaya et al. [42] synthesized a Schiff base oligomer of 2-[(4-morpholin-4-yl-phenyl)imino]methylphenol (2-MPIMP) and Oligomer–metal complex compounds from the reactions of *O*-2-MPIMP with $Cu^{2+}$, Co2+, $Cd^{2+}$, $Zn^{2+}$, $Pb^{2+}$ and $Zr^{4+}$ ions. Conductivity measurements of the Schiff base oligomer and its metal complexes were carried out and it was reported that when iodine was used as doping agent, conductivity of this oligomer and its metal complexes increased. The conductivity value of *O*-2-MPIMP–Zn compound was higher than *O*-2-MPIMP, *O*-2-MPIMP–Co, *O*-2-MPIMP–Cd, *O*-2-MPIMP–Cu, *O*-2-MPIMP–Pb and *O*-2-MPIMP–Zr compounds. The UV–vis absorption spectral values for the monomer and oligomer and oligomer–metal complexes are shown in Table 2. Also, electrochemical and optical band gap values of monomer, oligomer and oligomer–metal complex were determined. The results reported that, the oligomer–metal complexes had lower band gap than the monomer and oligomer because of the azomethine group, which is an electron-donor and this increases the HOMO more than the LUMO and therefore lowering the band gap. Since the observed band gaps are low these oligomer and oligomer–metal complex compounds were suggested as highly promising for photovoltaic applications. The thermal analysis showed that the monomer and oligomer were less stable than the oligomer–metal complex compounds.

Kaya et al. in another similar work [43], have synthesized Schiff base oligomer, oligo-2-[(phenylimino)methyl]phenol (*O*-2-PIMP) and its metal complexes oligo-2-[(phenylimino) methyl] phenol (*O*-2-PIMP) with $Co^{+2}$, $Ni^{+2}$, $Cu^{+2}$, $Cr^{+3}$, $Pb^{+2}$, and $Zn^{+2}$ ions. Their thermal, electrochemical, optical, and electrical properties were investigated. The voltammetry measurements and the UV–vis absorption spectra readings reported that, the oligomer had a lower band gap than 2-PIMP due to non-linear poly conjugation. The metal complex oligomers reported lower band gap values than the oligomer. The band gap values of monomer and oligomer were higher than those of oligomer–metal complexes due to the electron-donating property of the azomethine group. The conductivity measurement showed that the oligomer and oligomer–metal complex conductivity increased twice under doped condition. The conductivity values of *O*-2-PIMP–Cu complex compound were higher than *O*-2-PIMP, *O*-2-PIMP–Co, *O*-2-PIMP–Ni, *O*-2-PIMP–Cr, *O*-2-PIMP–Pb, and *O*-2-PIMP–Zn complexes. The observed band gap values and the conductivity of these compounds suggest that these oligomer and oligomer–metal complexes are highly promising for photovoltaic applications.

Pasa et al. [44] synthesized and characterized thio Schiff base ligands and their metal complexes with spectral techniques. The efficiency of the synthesized Schiff base ligand on Suzuki reactions was calculated. The transmission and absorbance spectra of the Ni (II) complex were investigated and the band gap values were determined by optical method. A photodiode was fabricated and the electrical characteristics were determined. The photovoltaic properties were examined using a solar simulator.

Kaya et al. [45] synthesized novel polyaminophenols and their metal complexes and confirmed their structure by FT-IR, UV–vis, $^{1}$H NMR, and $^{13}$C NMR techniques. The electrical properties such as conductivity of polymers were measured using the four-point probe technique. Fluorescence measurements were carried out in various solutions and optimum concentrations and maximal intensities were determined. The characterization of the newly synthesized polyaminophenols suggested that these compounds are good candidates for electronic, opto-electronic, and photovoltaic applications due to their polyconjugated structures.

As mentioned earlier, the ease of evaluation of photoelectrochemical properties and design of new organic dyes have created a great impact in the growth and interest in field of research of organic dyes [33]. Many researchers have developed newer materials, which although do not fulfill some of the requirements of a sensitizing dye, are suggested with potential ability to be used in photovoltaic devices. On these circumstances, papers based on Schiff bases with possible photovoltaics properties have also been reviewed.

Kaya et al. [46] synthesized soluble polyphenol derivatives containing azomethine bond. They synthesized four phenolic Schiff bases by condensation reaction of *o*-dianisidine with salicylaldehyde (2-HBADIAN), 4-hydroxybenzaldehyde (4-HBADIAN), vanillin (MHBADIAN) and 3-ethoxy-4-hydroxybenzaldehyde (EHBADIAN), and converted these monomers to their polyphenol derivatives via oxidative polycondensation reaction (OP). The synthesized compounds were characterized by determining the optical band gaps ($E_g$) by using UV–vis spectra of the materials, and the electrical conductivities of both doped and undoped states of the synthesized materials were also measured. The cyclic voltammetry readings were used to calculate the electrochemical band gap, and it was found that after the polycondensation process, the HOMO energy levels increased and the LUMO energy levels decreased, thus giving a lower electrochemical band gap. This property of the polymers facilitates a better electro-conductivity than the monomers. The electrical conductivity of the polymers suggested that they are semi-conductors, and the electrical conductivity of the polymer P-2-HBADIAN was 130 times higher undoped conductivity than the other synthesized polymers. Due to the semi-conductive nature and high thermal stability, they were suggested as electronic, optoelectronic, electro-active and photovoltaic applications.

Kaya et al. [47] synthesized a series of pyridine based Schiff bases (3-MAPDHB, 4-MAPDHB and 6-MAPDHB) with different methyl group, and converted to their polyphenol species (P-3-MAPDHB, P-4-MAPDHB and P-6-MAPDHB) via oxidative polycondensation reaction (OP). The synthesized compounds were characterized optical and electrical bangap, electrical conductivity and thermal stability. The UV–vis absorption spectra reported a lower optical bangap for the polyphenols than their monomers (Table 2.). The electrochemical band gap was determined by the cyclic voltammetry, and did agree with the optical band gaps. The polymers have a lower band gap value, because of their polyconjugated structure. The electrical conductivity study showed that the conductivity of the polymers could be increased by doping with iodine. The methyl substituent group in the P-3-MAPDHB, as a electron-donating group, improved the electrical conductivity of the polymer. The thermal stability results showed that the polyphenols had higher thermal stability than their monomers. The authors suggested that, due to the semi-conductive structure of the polyphenols, they could be used in electronic, optoelectronic, electro-active, and photovoltaic applications.

Kaya et al. [48] in their work, prepared a polymer of 4-[1-(4-hydroxyphenyl)ethylideneamino]phenol (4-HPEAP), a Schiff base substitute. Various studies were carried out on the effect of few parameters on the development of the polymer. Further the electrochemical property and electrical conductivity of the polymer were also determined. The optical and electrochemical band gaps results reported that the polymers had lower band gaps than the monomer. The UV–vis absorption spectra results are listed in Table 2. The electrical conductivity of P-4-HPEAP showed that the polymer was a typical semiconductor.

Demir [49] synthesized a novel polyphenol by oxidative polycondensation of 4-((2-phenylhydrazono)methyl)phenol (4-PHMP). The thermal properties and the electrochemical properties of the synthesized new polymer Schiff base were investigated. The electrochemical results reported that the polymer had a low band gap ($E'_g = 1.52$ eV). Since the lower band gap compounds are the most favourable for photovoltaic applications, it was suggested that this newly synthesized polymer could be used as an interesting candidate for solar-cell applications.

## 6. Conclusions

With the impressive progress in organic photovoltaic materials and devices, in last few years, the uses of Schiff bases and their metal complexes as photovoltaic material has gained interest due to their easy synthesize procedure and complexation with metal ions. This quality of Schiff bases and their metal complexes make them as a potential substitute for organic solar cells. Research has been done with Schiff bases and their metal complexes as sensitizing and acceptor materials in dye sensitized solar cells, but their application in organic solar cells are not familiar. The high thermal stability, wider range of absorption, lower band gap and good electrical conductivity properties promises the use of Schiff bases and their metal complexes as the future materials for organic photovoltaics.

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